Preparation, Characterization, and Prominent Thermal Stability of Phase-Change Microcapsules with Phenolic Resin Shell and *n*-Hexadecane Core

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ABSTRACT: Microcapsules with phenolic resin (PFR) shell and *n*-hexadecane (HD) core were prepared by controlled precipitation of the polymer from droplets of oil-in-water emulsion, followed by a heat-curing process. The droplets of the oil phase are composed of a polymer (PFR), a good solvent (ethyl acetate), and a poor solvent (HD) for the polymer. Removal of the good solvent from the droplets leads to the formation of microcapsules with the poor solvent encapsulated by the polymer. The microstructure, morphology, and phase-change property as well as thermal stability of the microcapsules were systematically characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimety (DSC), and thermogravimetric analysis (TGA). The phase-change microcapsules exhibit smooth and perfect structure, and the shell thickness is a constant fraction of the capsule radius. The initial weight loss temperature of the microcapsules was determined to be 330°C in N_2 and 255°C in air, respectively, while that of the bulk HD is only about 120°C both in air and N_2 atmospheres. The weight loss mechanism of the microcapsules in different atmosphere is not the same, changing from the pyrolysis temperature of the core material in N_2 to the evaporation of core material caused by the fracture of shell material in air. The melting point of HD in microcapsules is slightly lower than that of bulk HD, and a supercooling was observed upon crystallization. J Appl Polym Sci 104: 2799–2806, 2007

Key words: phase-change microcapsule; phase separation; phenolic resin; thermal stability

INTRODUCTION

The field of microencapsulation emerged in 1950s and got rapidly expanded in 1970s, originally directing toward entrapping solids, liquids, or gases into polymeric shells. From 1990s, microcapsules have been developed, studied, and used by scientists and engineers of different backgrounds throughout the chemical and life sciences, biotechnology, medicine, and related industries because of the many advantages afforded by these encapsulated systems.[1,2] A wide range of core materials have been encapsulated, including adhesives, drugs, agricultural aids, paper coating, enzymes, salts, dyes, electronic ink, fragrant oils, long chain normal alkanes, waxes, etc.[3–8]

Since the 1990s, microencapsulated phase-change materials (MPCM) have attracted more and more attention. Since phase-change material (PCM) can absorb, store, and dissipate large amounts of latent heat in its phase-change temperature range, MPCMs have been widely used in many practical fields, such as heating and air conditions of building,[9] thermal insulation materials,[10] solar and nuclear heat storage,[11,12] thermal adaptable fibers,[13] and so on. Many methods have been tried to prepare microcapsules with liquid/solid core and solid shell. The most commonly used method is the interfacial step-growth polymerization, i.e., one monomer dissolved in dispersed phase reacts with another monomer in continuous phase at the oil–water interface to form polymer shell.[14–17] As the polymerization reaction proceeds, the reaction rate decreases, leading to a thinner shell. Furthermore, partial monomer will inevitably remain in the core as impurity that also exists when vinyl monomer polymerizes in emulsion droplet.[18–20] Another method is the controlled precipitation of polymer from the continuous phase of an emulsion to surround the droplets of the dispersed phase,[4,6,21] resulting in the shell thickness lack of uniformity and nucleation independently. Internal phase separation is

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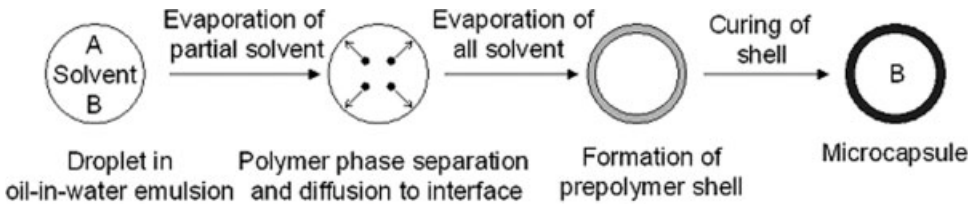

Figure 1 Schematic illustration for microcapsule formation: A, polymer (PFR); B, poor solvent for polymer (HD). ''Solvent:'' good solvent for PFR and HD.

another method to prepare shell/core materials.[4,22] When compared with the method mentioned earlier, this method can avoid the drawbacks of interfacial step-growth polymerization and lead to microcapsules with constant volume fraction of shell material.

When used as thermal adaptable fibers, heat-resistance of MPCM is crucial.[23] Selecting appropriate shell materials are important for improving thermal stability of the microcapsules. A series of polymers have been used as the shell materials of MPCMs, such as melamine-formaldehyde,[23,24] crosslinked nylon,[25] urea-formaldehyde,[4,23,26] polyurethane,[14] and gelatin-formaldehyde,[11] but usually the microcapsules were used at lower temperature. This limits the application of these materials. As is known, owing to its aromatic structure, phenolic resin (PFR) is of better thermal stability when compared with any of the other polymers mentioned earlier.[27] To the best of our knowledge, no work has been reported on the preparation of PCM with PFR as shell.

In this study, through the method called ''internal phase separation'' within the droplets of an oil-in-water emulsion,[22] we prepared MPCM with PFR shell and hexadecane (HD) core, and subsequently investigated the thermal property of the microcapsules. The process for the formation of the shell/core structure is illustrated in Figure 1. Although a series of thermoplastic polymer shells have been prepared by this method,[22,28–30] to the best of our knowledge, no report has appeared on the preparation of thermoset polymer microcapsule. The process to prepare microcapsule with PFR shell is different from that with thermoplastic polymer shell because of the much lower molecular weight of PFR. The low molecular weight of PFR has both advantages and disadvantages for the preparation of the microcapsule by internal phase separation. The advantage is that lower molecular weight decreases the viscosity of the droplets, so during phase separation, the polymer diffuses to the interface easily; the disadvantage is that the shell strength was not high enough before curing for maintaining stable morphology. In this work, PCM with PFR shell and HD core was successfully prepared through choosing appropriate emulsifier and solvent-removing rate as well as curing fashion.

EXPERIMENTAL

Materials

Phenol, formaldehyde (37% aqueous solution), and hexamethylenetetramine were purchased from Beijing Yili Chemicals Factory, China, and used to synthesize the shell material. *n*-HD (Acros, 97%) was used as core material. Gum arabic and sodium dodecyl sulfate (SDS, Tianjin Kemiou Chemical Regents Factory, China) were used as emulsifiers. The solvent used were supplied by Beijing Chemicals Factory. All the reagents were of analytical grade and were used as received. Doubly deionized water was used as aqueous medium.

Synthesis of PFR

The PFR used as the shell material was synthesized and purified as described by Brode et al.[31] In a typical synthesis, the mixture of phenol (50 g), aqueous formaldehyde (50 g), hexamethylenetetramine (4.5 g), gum arabic (0.5 g), and water (27.5 g) was charged into a three-necked flask equipped with a mechanical stirrer, a thermometer, and reflux condenser. The reaction temperature was maintained at 85°C in a water bath for 70 min. The obtained particulate resole was collected by filtration, washed with distilled water for three times, and dried at 40°C for 2 h.

Microcapsule preparation

Different amounts of PFR were added to adjust the shell thickness. PFR was firstly dissolved in the mixture of ethyl acetate (24 g) and acetone (6 g), and then HD (1 g) was added. A 20-mL aqueous surfactant solution was charged into a 100-mL three-necked round-bottomed flask equipped with a mechanical stirrer. The organic solution was added to the aqueous surfactant solution, and the mixture was emulsified mechanically at a rate of 3000 rpm to form an oil-in-water emulsion. After agitation, which lasted for 1 h at 25°C, the diluted emulsion was rotary evaporated for 40 min at 30°C followed by transferring into a Teflon-lined autoclave and treated at 150°C for about 6 h, and then allowed to cool down to room temperature

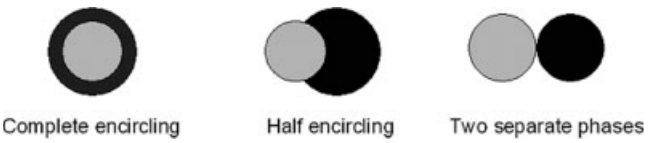

Figure 2 Three possible morphologies formed by internal phase separation of oil-in-water emulsion.

gradually. The resultant microcapsule dispersion was collected with centrifugation, and then washed with distilled water, ethanol, and ethyl acetate, and finally dried in vacuum oven for 10 h at 60°C.

Characterization

SEM

Scanning electron microscope (SEM, HITACHI S-4300, Japan) was used to investigate the final microcapsule morphology and size. One drop of the microcapsule dispersion was placed on a stainless steel SEM stub and allowed to air-dry overnight. To determine the shell thickness, the microcapsules were fractured under liquid nitrogen with a glass rod. Before observation, the dried sample was coated with a layer of gold with a thickness of $\sim$ 10 nm.

FTIR

The chemical structure of microcapsule and the shell polymer was analyzed using Fourier transform infrared spectroscopy (FTIR, PerkinElmer, IR2000). The spectra were collected by signal averaging of 32 scans at a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}.

Phase-change property and thermal stability

A differential scanning calorimeter (Mettler-Toledo, DSC822e) was used to evaluate the thermal properties of the microcapsules containing PCM. The core material content was estimated from the heat of phase change. The determination temperature varied from −35 to 50°C at a heating rate of 2°C/min. The mechanism of weight loss was also investgated by DSC. The determination temperature was ranged from 25 to 450°C at a heating rate of 10°C/min. To get detailed information of the microcapsule thermal stability, the samples were measured under either N_2 or air atmosphere.

The weight loss temperature of the microcapsules was investigated by using a thermogravimetric analysis (TGA, Netzsch STA409pc). The sample was heated at a heating rate of 10°C/min both in air and under N_2 atmosphere.

RESULTS AND DISCUSSION

When two dissimilar phases (A and B) separate from each other by evaporating the solvent from the droplets in oil-in-water emulsion, there is only one thermodynamic equilibrium configuration of A spreading on B, though there exist three possible morphologies of the phase-separation result (Fig. 2).[29] The extent of spreading is determined by the rate of phase separation, which can be controlled by the rate of solvent evaporation.[5] In a droplet mixture consisting of PFR, HD, and solvent, phase separation occurs because of the removal of the solvent. The evaporation rate of the

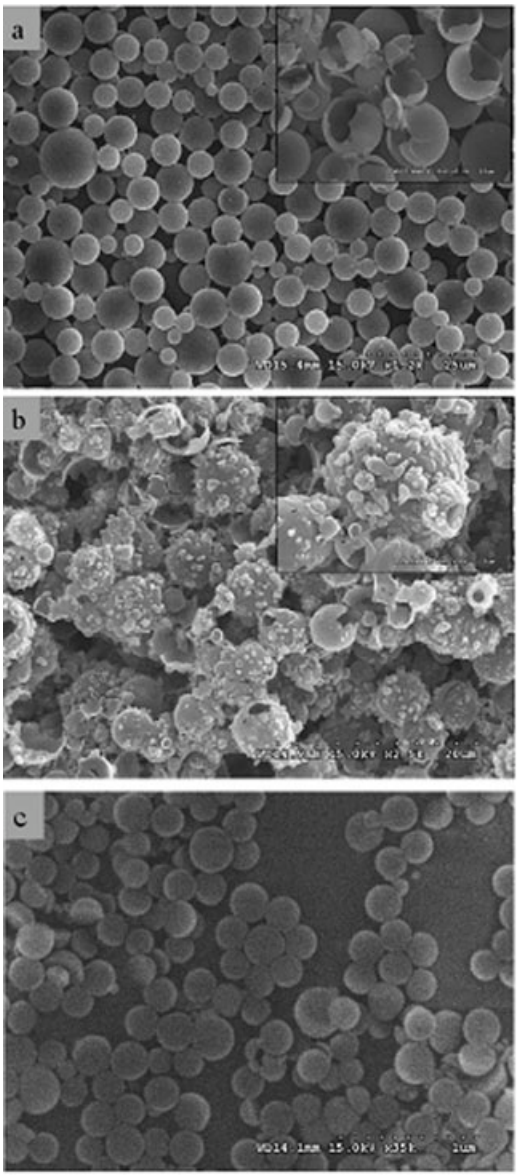

Figure 3 SEM images of PFR shell/HD core microcapsule produced from emulsion containing 3.13 wt % PFR in the oil phase, gum arabic as emulsifier, and different amounts of SDS: 0 (a); 0.1 (b); and 0.2 wt % (c). Insets are the images of microcapsule fractured.

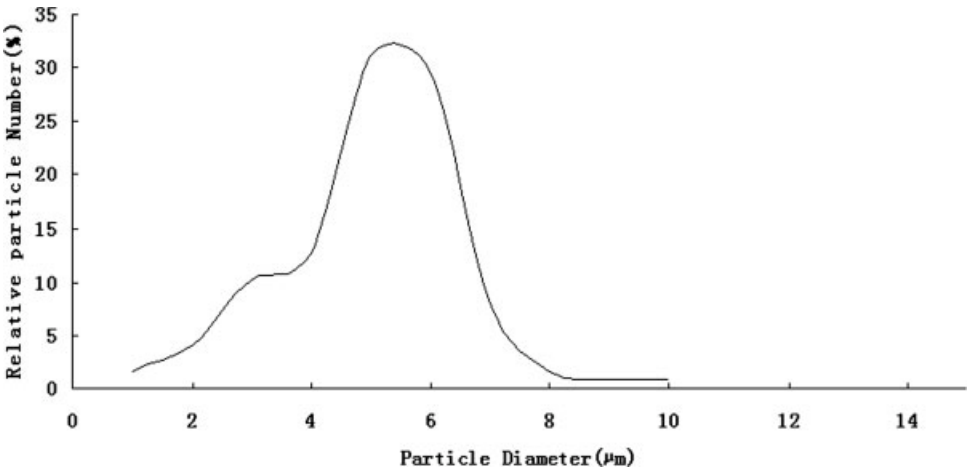

Figure 4 Particle size distribution of microcapsules produced from emulsion containing 3.13 wt % PFR, gum arabic as emulsifier.

solvent and the interfacial tension are key factors to the phase separation. If the two factors are suitable, a spherical droplet of HD becomes coated with a highly uniform layer of the PFR. Otherwise, the polymer concentration is also important to control the shell thickness of microcapsules. The agitation rate, surfactant concentrations, and organic phase volume can also influence the mean particle diameter, size distribution as well as the shell thickness.[32]

Microcapsules morphology

The effect of surfactants

Gum arabic was used to disperse the oil phase into water at a concentration of 2 wt % in aqueous solution. We tried to emulsify the oil using PVA, CTAB, or SDS to obtain stable emulsion, and found that only gum arabic is suitable emulsifier for our research system. To investigate the effect of surfactants on microcapsule morphologies, different amounts of SDS were added with gum arabic. Figure 3 shows the SEM micrographs of the microcapsules containing 3.13 wt % PFR in oil phase. When only gum arabic was used [Fig. 3(a)], the capsules are clearly spherical with a smooth surface and average diameter of ~5 μm (Fig. 4). To investigate the internal structure of the microcapsules, the particles were fractured in liquid nitrogen with a glass rod. Hollow structure with a single internal cavity is found [Fig. 3(a), inserted picture], indicating the formation of shell/core microcapsules. FTIR spectra of HD, PFR, and HD-contained microcapsule are shown in Figure 5. The strong adsorption peaks at 2924–2854 cm^{-1} are associated with the aliphatic C—H stretching vibration of HD, and the adsorption peak at 721 cm^{-1} is associated with the in-plane rocking vibration of CH_2 group. This means that HD was successfully microencapsulated inside PFR shells. The microcapsule structure can also be confirmed by DSC thermograms (Fig. 6), i.e., the capsulated HD shows a phase change near the same temperature range as that of the bulk material.

When 0.1 wt % SDS in water was added with 2 wt % gum arabic, the microcapsules obtained were polydispersed in size and the capsules with small diameters were adsorbed on the surface of the big capsules [Fig. 3(b)]. It was concluded that from the microcapsule fractured, hollow structure was also formed. However, when the amount of SDS was increased to 0.2 wt %, particle diameter decreases much as shown in Figure 3(c). But encapsulation was failed, meaning that PFR and HD nucleated independently in the polymerization process. The HD droplets were removed by washing with ethyl acetate, while only PFR solid

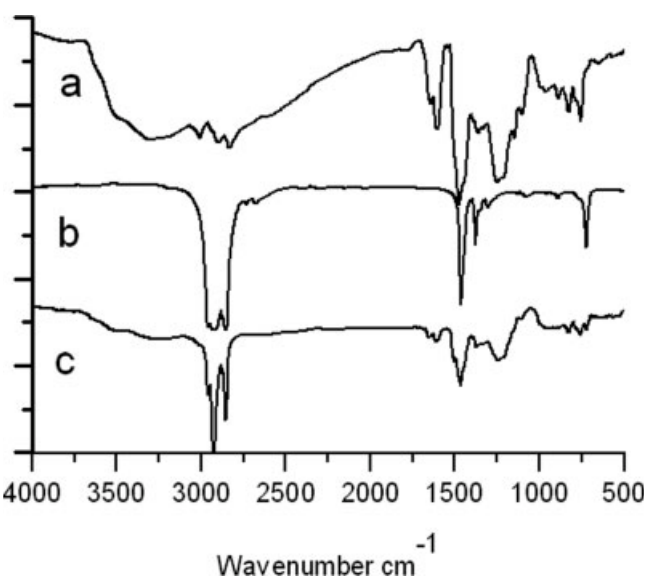

Figure 5 FTIR spectra of PFR shell/HD core microcapsules prepared with 3.13 wt % PFR added: phenolic resin (a); hexadecane (b); and microcapsule (c).

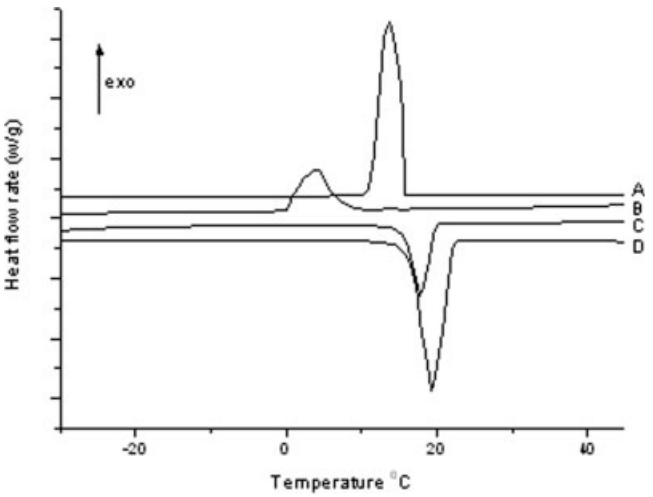

Figure 6 DSC thermograms of bulk hexadecane and microcapsule prepared with 3.13 wt % PFR added: (a) cooling curve of bulk HD; (b) cooling curve of HD contained microcapsule; (c) heating curve of HD contained microcapsule; and (d) heating curve of bulk HD.

particles remained. The failure of encapsulation can be confirmed by DSC thermographs on which no endothermic peak was observed near the temperature of phase change (not shown here). The difference in morphology may result from the addition of SDS. It decreased the oil/water interfacial tension too much, which would decrease the driving force of polymer diffusion to the oil/water interface. As the interface tension changed with the type and concentration of surfactant, thermodynamic morphology of PFR spreading on HD turned from complete-circling to two-separate phases (Fig. 2).

Effect of solvent removing rate

The microcapsules in Figure 3(a) were prepared by rotary evaporating for 40 min at 30°C after an emulsification period of 60 min. It was reported that the microcapsule surface is quite uneven when prepared by evaporating solvent through stirring the emulsion at 200 rpm for 24 h.[22] The difference in morphologies is explained as follows: during the long-time stirring after emulsification, the solvent evaporates much more slower from the droplets than from the rotary evaporation. Slow polymer-phase separation yields an initially thin shell, resulting in further shrinkage as more solvent is removed.

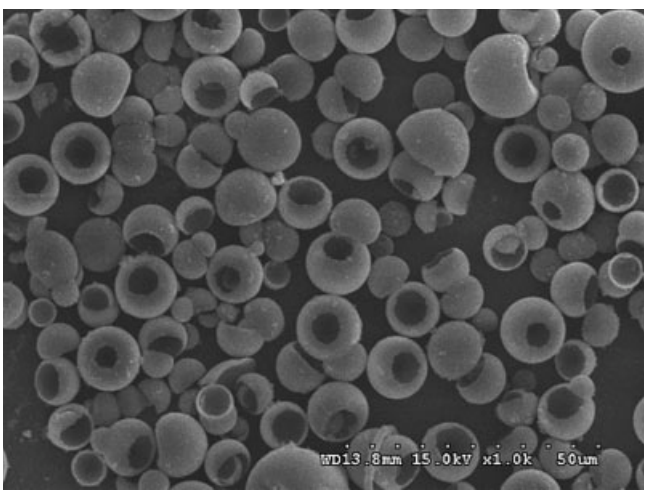

Figure 7 SEM image of microsphere prepared by rotary evaporating at 40°C.

In this work, when evaporating solvent was performed by rotary evaporation for 30 min at 40°C (almost the same vacuum tightness as that at 30°C) after the emulsification process, hollow PFR microspheres with a single hole in the shell were obtained (Fig. 7). The formation mechanism can be explained as follows. As the solvent evaporates, phase separation occurs and the polymer diffuses to the inner interface of the droplets, resulting in the decreasing of the interfacial tension.[33] When the solvent evaporates slowly (at 30°C) by rotary evaporation, the polymer separated out and gradually self-assembled at the inner interface, leading to the formation of a PFR shell. However, when the solvent removal temperature rises up to 40°C, the phase separation of PFR is so fast that the polymer does not have enough time to form an even shell on the interface. The region where the adsorption of polymer is insufficient would be occupied by the surfactant molecules aggregates, as a result, a hole is formed in the shell.

Effect of polymer concentration

Figure 1 shows that the composition of each droplet should be the same as that of the parent organic solution. Since a single microcapsule originates from each droplet, the ratio of capsule shell thickness to radius could be concluded from eq. (1) by the amounts of PFR and HD added.[22]

$$t/r = 1 - \left(1 - \Phi_p\right)^{1/3} \quad (1)$$

where t and r were the shell thickness and radius of the microcapsule, respectively, Φ_p was the ratio of the shell volume to the total volume of microcapsule. To validate relation of the amount of polymer used for the formation of microcapsules with resultant shell thickness, different amount of PFR (1.27, 3.13, and 6.06 wt %) were added in the oil phase. The shell thicknesses (t/r) of these capsules predicted from eq. (1) are 6.9, 14.4, and 23.0%, respectively. Fracturing the microcapsule, the shell thickness can be directly confirmed from SEM micrographs (Fig. 8). It is obvious that the experiment was in good accordance with the theoretical calculation. The shell thicknesses are almost uniform and agree well with the amounts of PFR added. Figure 8(a) shows that the microcapsules

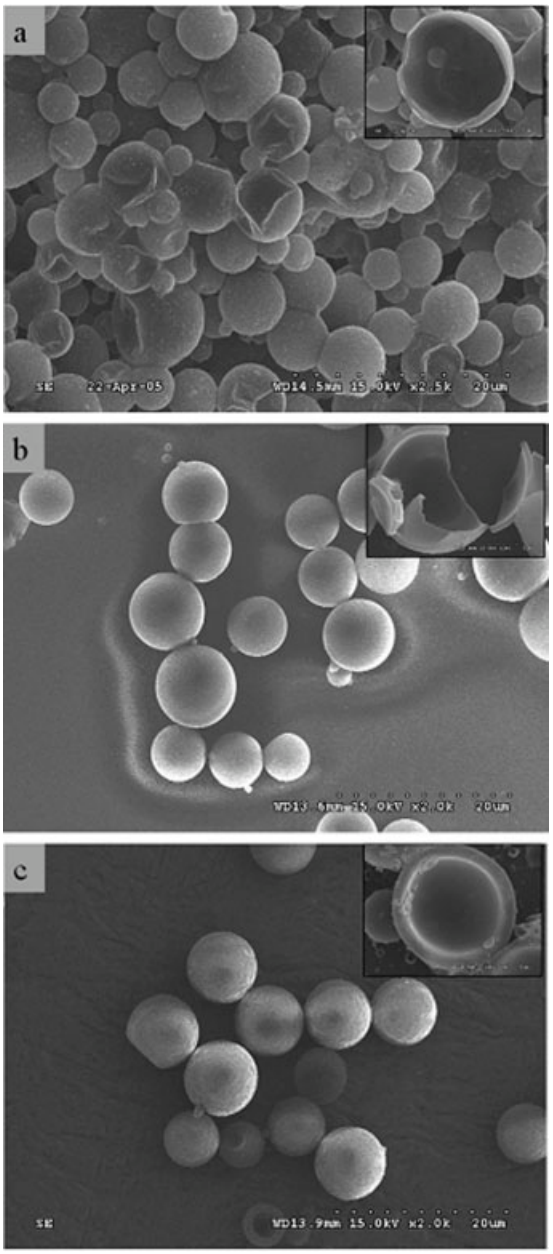

Figure 8 SEM images of microcapsules produced from different amounts of PFR added: (a) 1.25, (b) 3.13, and (c) 6.25 wt %. Insets are the cross section of the microcapsules.

with thinner shell are easy to fracture and have not enough strength to protect the core material from escaping. When increasing the amount of PFR, the shell thickness increased gradually [Fig. 8(b,c)]. Therefore, predicting from eq. (1), microcapsule with designed shell thickness can be prepared by controlling the amount of polymer added.

Thermal stability

The thermal stability of the microcapsules containing HD was evaluated using TGA in N_2 and air atmosphere, respectively. TGA thermograms of HD, cured PFR, and HD-containing microcapsule are presented in Figure 9. From the curves, it is shown that the initial weight loss temperatures of bulk HD are all 120°C in different atmosphere, while those of microencapsulated HD in N_2 and air are determined to be 330 and 255°C, respectively.

The mechanisms of weight loss in air and N_2 atmosphere are different. In N_2 atmosphere, the polymer shell is of good thermal stability, meaning that the shell can protect the core material from escaping. When the temperature increased to 330°C, the encapsulated HD began to be pyrolyzed. As a result, the pressure of shell wall increased and the shell was fractured. This could be concluded by an endothermic process determined by DSC [Fig. 10(A)]. In air atmosphere, however, the microcapsules showed a little

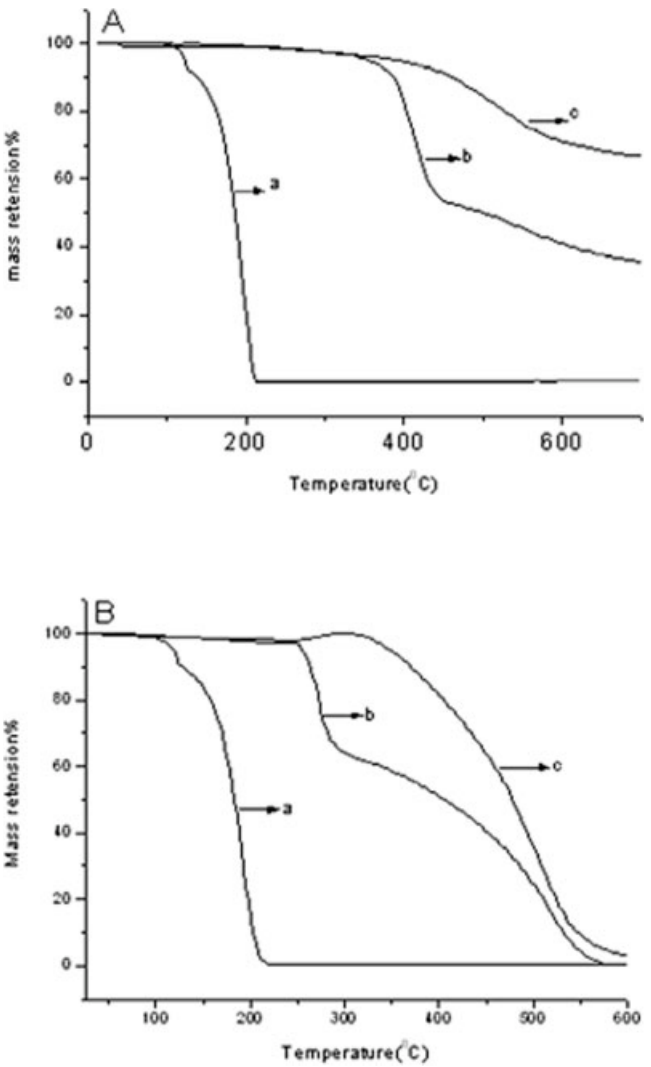

Figure 9 TGA thermograms of HD, PFR, and microcapsule prepared with 3.13 wt % PFR added in different atmosphere. (a) HD, (b) microcapsule, and (c) PFR; (A) in N_2 and (B) in air.

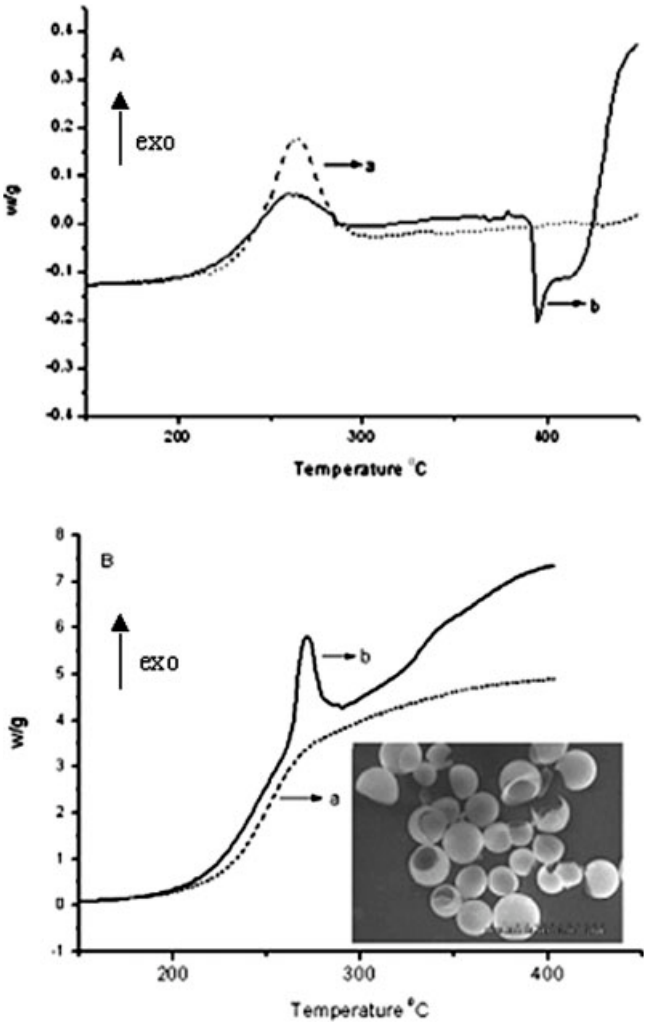

Figure 10 DSC thermograms of curing PFR and microcapsule prepared with 3.13 wt % PFR added in N_2 (A) and air (B) atmosphere. (a) PFR and (b) microcapsule. The picture inserted is the SEM image of the microcapsules treated at 250°C for 10 min in air atmosphere.

weight loss before a breakdown happened. The microcapsules almost lost all the HD encapsulated in a few minutes from 255°C on accompanying with a visible exothermic process shown on DSC curve [Fig. 10B(b)]. On the same situation, the bulk PFR just began to be oxidized and the resin had slightly increased in weight. Treating the microcapsules at 250°C for 10 min in air atmosphere, it is found that most of the microcapsules were broken [SEM inserted in Fig. 10(B)], indicating that oxidation decreases the strength of the shell and results in the shell easily to be fractured. As temperature further increased, HD diffused out of the fractured shell and contacted air, subsequently caught fire immediately. These continuous changes led to an exothermic process and fast weight loss. This phenomenon had also been observed in previous study on microencapsulated *n*-octadecane.[23] Therefore, thermal stability of the microcapsules depends on the atmosphere, the heat-resistance of the shell polymer, and the pyrolysis temperature of the core material. In N_2, owing to the perfect thermal stability of shell polymer, the microcapsules are thermal stable up to the pyrolysis temperature of HD. In air, however, oxidization can decrease the shell strength, which decides the weight loss temperature of microcapsules.

Phase-change property

Being microencapsulated, the PCM (HD) provided a larger heat transfer area and a limited heat transfer space, leading to a great difference of the thermal behavior between the bulk HD and microencapsulated HD. The phase-transition temperature and the energy storage or release capacity of the microcapsules are shown in Table I.

From Table I, it can be seen that the melting points of all the samples are lower than that of bulk HD, though showing a slight increase with the increase of PFR content in microcapsules. Simultaneously, when $m_{PFR} = 0.4$ g, the efficient of encapsulation is relatively low since the fusion latent heat is only 7.48 J g^{-1}. With higher content of PFR in the microcapsules, though the relative content of HD is lowered, the latent heat of fusion is increased much and the efficiency of encapsulation is greatly improved. This can be clearly visualized in Figure 8. When the ratio of PFR is low, the microcapsule forms a thinner shell with poor strength. Most of the capsules are easily fractured, leading to the escaping of PCMs. With the increase of PFR content in the microcapsules, a thicker shell is formed and HD is encapsulated more perfect, which will increase the latent heat of fusion.

Table I also shows that the crystallization temperature of encapsulated HD is much lower than that of bulk HD, though only one crystallization peak appears in the DSC cooling curve, which is different from the previous study where two crystallization peaks were observed.[23,34] It is demonstrated that supercooling crystallization is caused by the decrease in the number of nuclei in each microcapsule when the diameters are smaller than 100 μm. Furthermore, the crystallization temperature decreases with the diameter. To prevent supercooling crystallization, many materials are added with the core oil as nucleating agents to promote the heterogeneous nucleation.[35]

CONCLUSIONS

HD microcapsules with PFR shell have been prepared by internal phase separation from emulsion droplet. The shell thickness is easily adjusted by varying the ratio of shell (PFR) to core (HD), and can be estimated from SEM micrographs. When compared with the bulk HD, the thermal stability of HD in the microcap-

TABLE I
Thermal Properties of Hexadecane and Microencapsulated Hexadecane

PFR (g)	HD (g)	T_m[a] (°C)	ΔH_F[b] (J g^{-1})	T_C[c] (°C)	ΔH_C[d] (J g^{-1})	Content of PCM[e] (%)
0	1	19.29	256.69	13.60	256.70	100
0.4	1	16.96	7.48	1.70	7.45	3
1	1	17.29	98.08	3.91	96.49	38
2	1	18.23	85.29	3.99	86.05	33

[a] The peak value on the DSC heating curve.
[b] The enthalpy obtained from DSC heating curve.
[c] The peak value on the DSC cooling curve.
[d] The enthalpy obtained from DSC heating curve.
[e] Phase-change material.

sules is greatly improved both in air and N_2 atmosphere. Protected by the PFR shell, the PCM (HD) can be tolerant to 330°C in N2 and 255°C in air, respectively. The mechanisms of weight loss are completely different in dissimilar environment. In N_2, owing to the good thermal stability of PFR, the microcapsule is thermal stable up to the pyrolysis temperature of HD. In air, however, the shell material is oxidized with temperature increasing and its strength decreases correspondingly. So the thermal stability of the shell is most important. The melting point of HD in microcapsule is slightly lower than that of pure HD, while its crystallization temperature decreases much compared to bulk material, causing the so-called ''supercooling'' phenomenon.

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